ChE-402: Diffusion and Mass Transfer

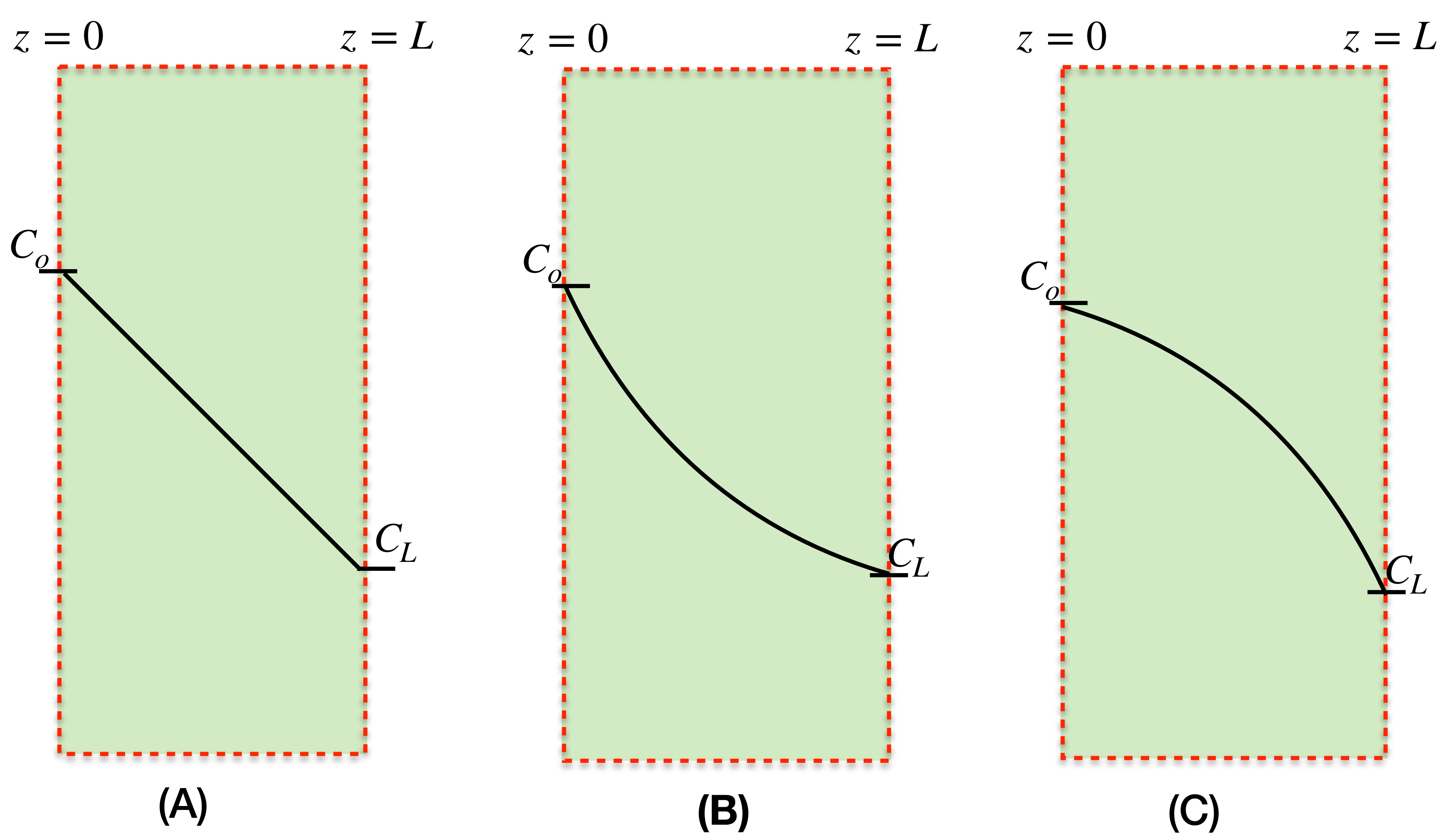
Lecture 3

Concentration-dependent diffusion coefficient

$$D = D(c)$$

$$J = -D\frac{dC}{dz}$$

with D decreasing at higher concentration. Which one is correct concentration profile for thin film?



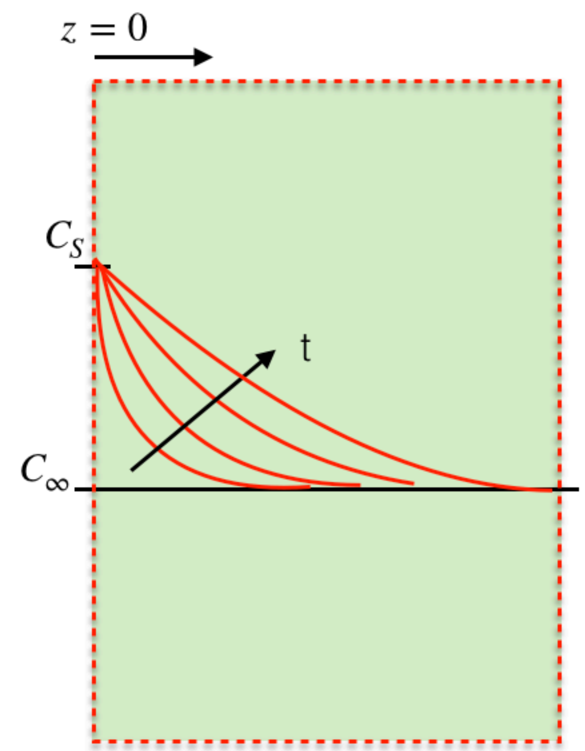
Did you observe?

Cooking times in minutes for a single brand of pasta are as follows

Capellini	2
Linguini	11
Fettucini	7
Spaghetti	12
Lasagna	9

Since all are made from the same flour, why are they different?

$$\frac{C - C_S}{C_\infty - C_S} = erf\,\zeta \;=\; \frac{2}{\sqrt{\pi}}\int_0^{\zeta} \exp(-s^2)ds$$



Intended Learning Outcome

To formulate a general way to solve problems when mass transport by convection also takes place along with diffusion

Diffusion with fast chemical reaction

Example: Dyeing of wool; reacted dye is immobile (does not move)

$$c_1 \rightleftharpoons c_2 \qquad c_2 = Kc_1$$

Initial condition: $t < 0, \; c_1 = c_{1,\infty}, \quad c_2 = 0$

At t= 0, the concentration at left face (z= 0) is raised to $c_{1,s}$

Chemical reaction: Solute (1) reacts with slab to form an immobile product (2).

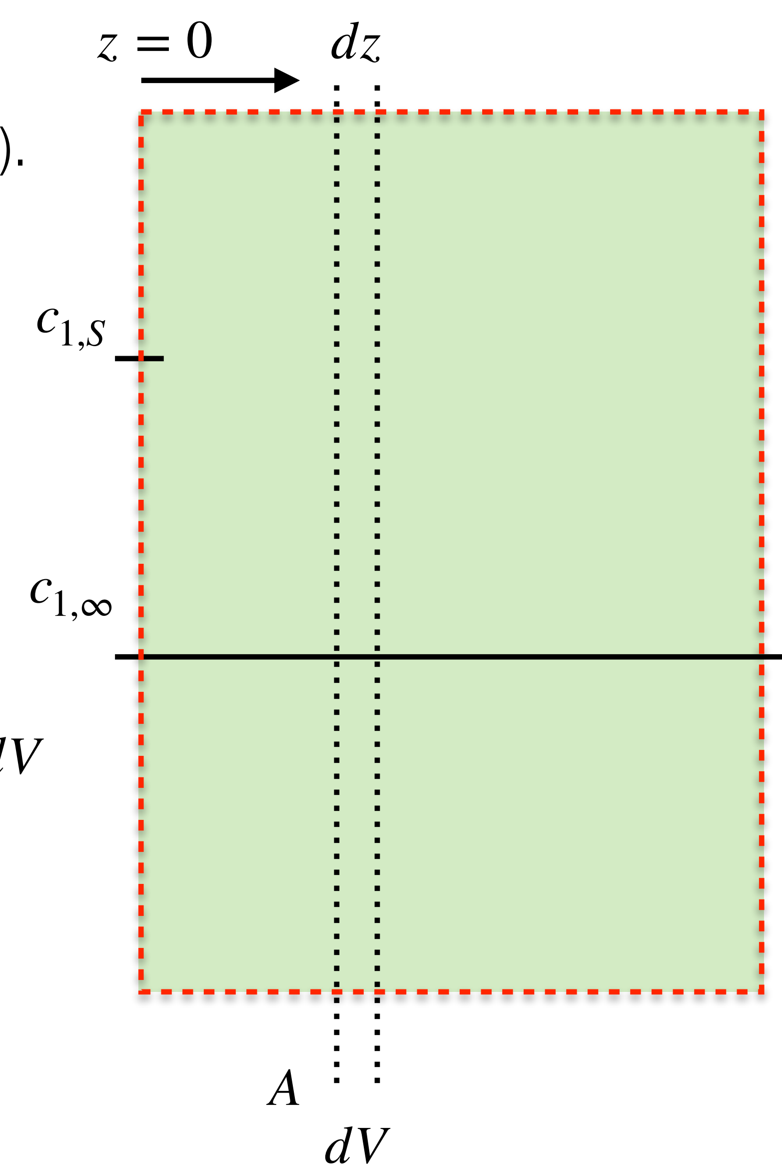
The reaction is fast but at equilibrium with constant K.

Define your system:

Define an elemental volume to do mass balance:

Apply mass balance for solute (1): dV = Adz

$$\overset{o}{Accumulation} * dV = \overset{o}{Flux}\,|_{in} * A - \overset{o}{Flux}\,|_{out} * A + \overset{o}{Generation} * dV - \overset{o}{Consumption} * dV$$



Diffusion with fast chemical reaction

Apply mass balance for product

$$\overset{o}{Accumulation} * dV = \overset{o}{Flux}\,|_{in} * A - \overset{o}{Flux}\,|_{out} * A + \overset{o}{Generation} * dV - \overset{o}{Consumption} * dV$$

Apply equilibrium condition

$$c_2 = Kc_1$$

$$\frac{\partial c_2}{\partial t} = r = K\frac{\partial c_1}{\partial t}$$

$$\frac{\partial c_1}{\partial t} = D_1\frac{\partial^2 c_1}{\partial z^2} - r$$

Substitute r in first equation

$$\frac{\partial c_1}{\partial t} = D_1\frac{\partial^2 c_1}{\partial z^2} - r$$

$$\frac{\partial c_1}{\partial t} = D_1\frac{\partial^2 c_1}{\partial z^2} - K\frac{\partial c_1}{\partial t}$$

$$\frac{\partial c_1}{\partial t} = \frac{D_1}{1+K}\left(\frac{\partial^2 c_1}{\partial z^2}\right)$$

Diffusion with fast chemical reaction

$$\frac{\partial c_1}{\partial t} = \frac{D_1}{1+K}\left(\frac{\partial^2 c_1}{\partial z^2}\right)$$

$$\frac{\partial c_1}{\partial t} = \bar{D}\left(\frac{\partial^2 c_1}{\partial z^2}\right) \qquad \bar{D} = \frac{D_1}{1+K}$$

$$\frac{c_1 - c_{1,S}}{c_{1,\infty} - c_{1,S}} = erf\ \zeta \qquad \zeta = \frac{z}{\sqrt{4\bar{D}t}}$$

$$J = -\bar{D}\frac{\partial c}{\partial z} = -\sqrt{\frac{\bar{D}}{\pi t}}\ (c_\infty - c_S)\ \exp\left(-\frac{z^2}{4\bar{D}t}\right)$$

EPFL

When will you reach steady-state?

$$\frac{\partial c_2}{\partial t} = r = K\frac{\partial c_1}{\partial t}$$

$$\frac{\partial c_1}{\partial t} = D_1\frac{\partial^2 c_1}{\partial z^2} - r$$

When convection is also present

Convection is characterized by bulk directional movement of the fluid.

Convection

There is a bulk motion

There is a direction

Sum of convective flux may not be zero

Can be treated as moving frame of reference

Diffusion

There is no bulk motion

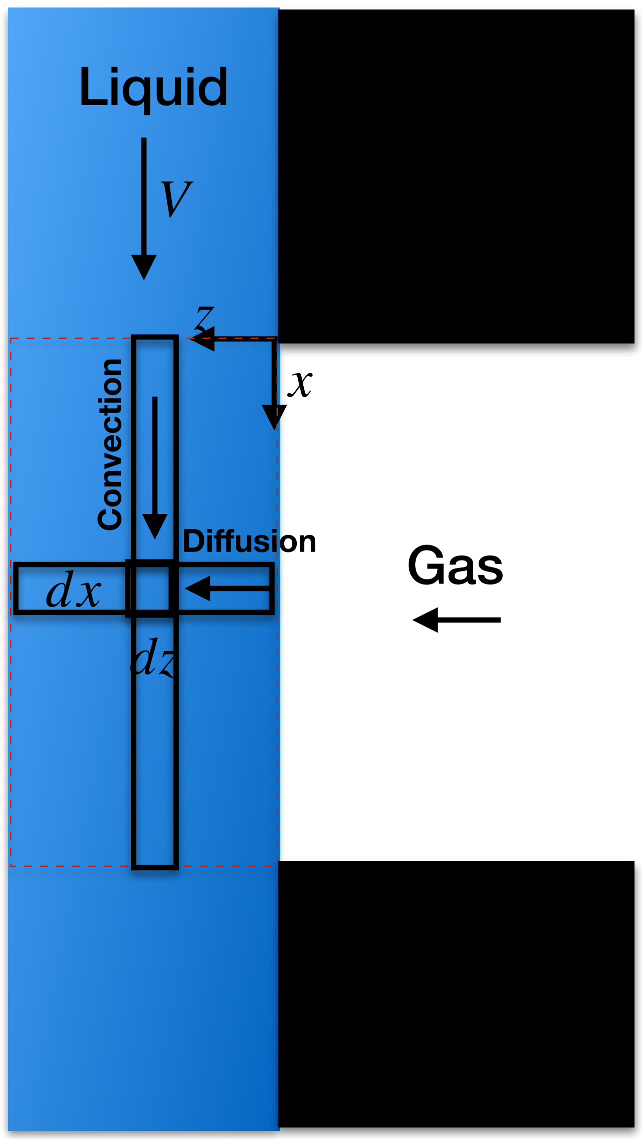
Always stochastic (random walk)

Sum of diffusive flux (two or more mobile components) is always zero

Role of convection:
Steady-state gas diffusion in falling film:

Gas is being absorbed in falling liquid film flowing down with a velocity V. Absorbed gas diffuses from the gas-liquid interface (concentration c_s) into the interior of the liquid film (concentration zero initially). Liquid film thickness is semi-infinite. A constant flow velocity can be assumed. Our goal is to calculate the concentration of gas as a function of position (x and z) in liquid

Define your system - Region where diffusion is taking place



Define an element to do mass balance

Boundary conditions

$$x = 0; \quad c = 0 \quad \text{for all z}$$

$$x > 0; \quad c\,|_{z=0} = c_S \quad \text{for all x}$$

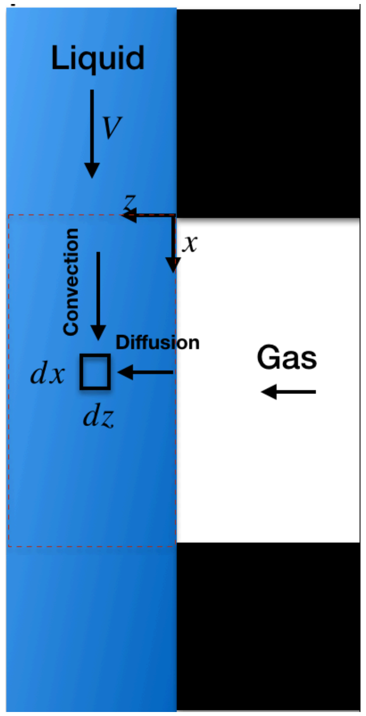
$$c\,|_{z=\infty} = 0$$

Steady-state gas diffusion in falling film

Apply mass balance for solute

Area for diffusion = Wdx   Area for convection = Wdz

$$\overset{o}{Accumulation} * (dxdzW) = \overset{o}{Flux}\,|_{in} * (Wdx) - \overset{o}{Flux}\,|_{out} * (Wdx) + \overset{o}{Generation} * (dxdzW) - \overset{o}{Consumption} * (dxdzW)$$



Rearranging

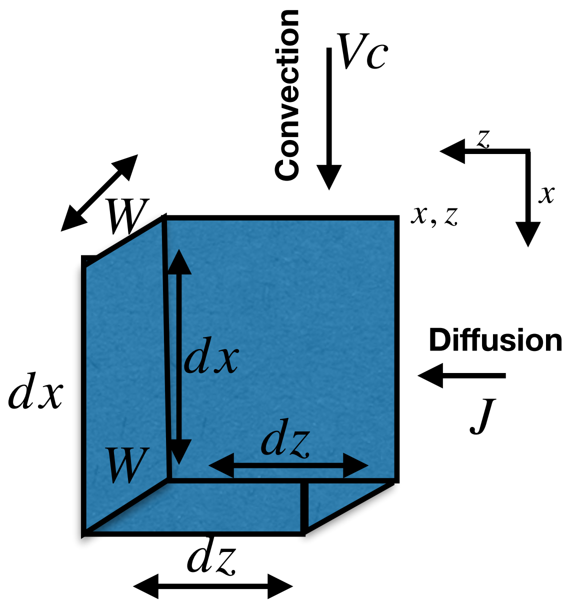
$$-\frac{Vc\,|_x - Vc\,|_{x+dx}}{dx} = \frac{J\,|_z - J\,|_{z+dz}}{dz}$$

$$\Rightarrow V\frac{dc}{dx} = -\frac{dJ}{dz}$$

Applying Fick's law

$$\Rightarrow V\frac{dc}{dx} = D\frac{d^2c}{dz^2}$$

$$\Rightarrow \frac{dc}{d\left(\frac{x}{V}\right)} = D\frac{d^2c}{dz^2}$$



Gas diffusing in falling film

$$\frac{dc}{d\left(\frac{x}{V}\right)} = D\frac{d^2c}{dz^2}$$

$$\zeta = \frac{z}{\sqrt{4D\frac{x}{V}}}$$

Boundary conditions

$x = 0;\ c = 0$ for all z

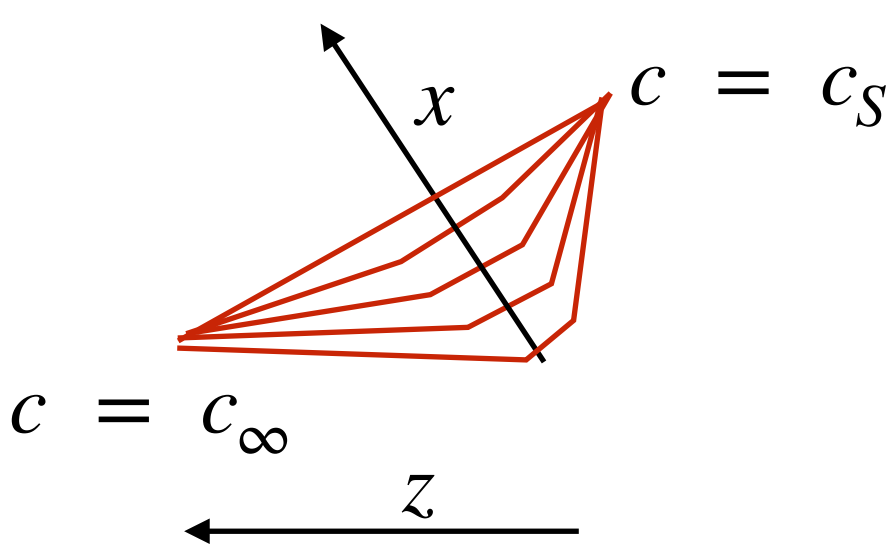
$x > 0;\ c\,|_{z=0} = c_S$ for all x

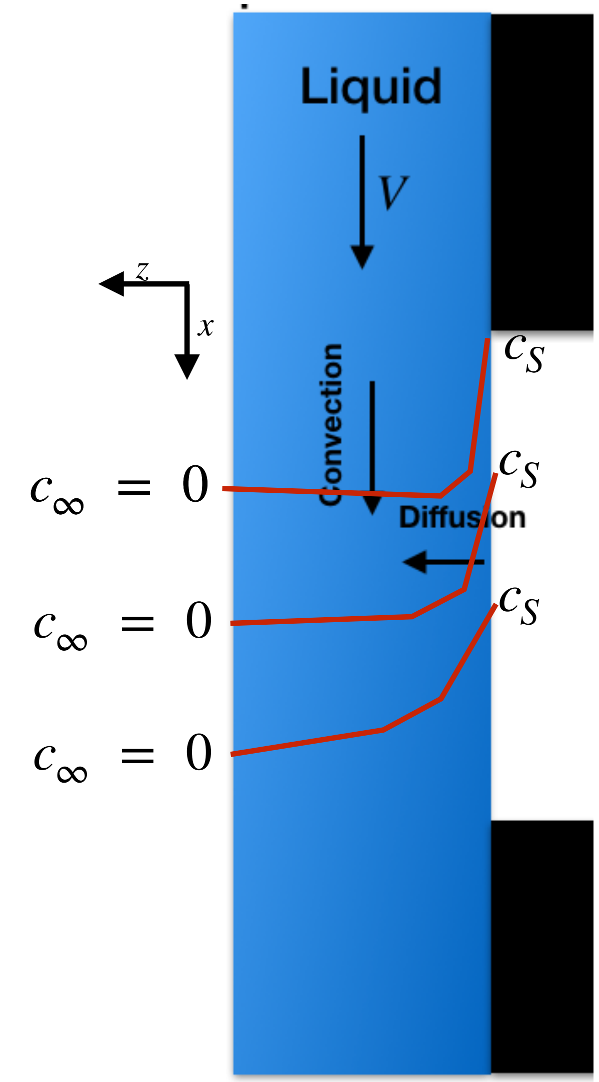
$c\,|_{z=\infty} = c_\infty = 0$

$c\,|_{\zeta=\infty} = 0$

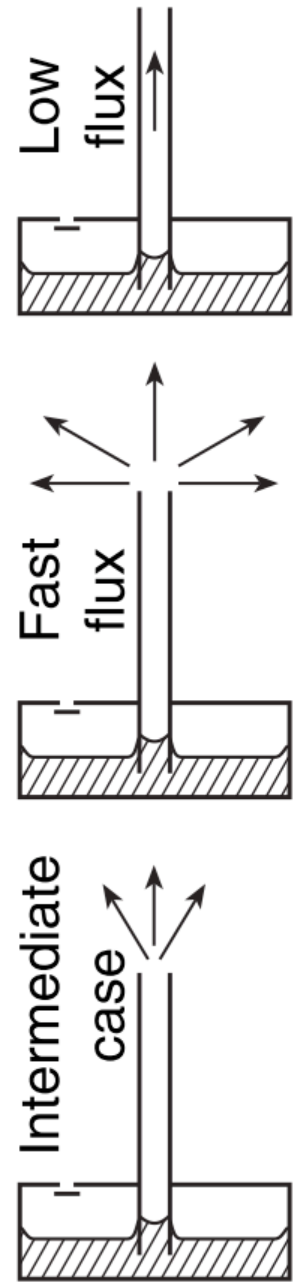
$c\,|_{\zeta=0} = c_S;$

$$\frac{c(z,x) - c_S}{c_\infty - c_S} = erf\ \zeta \qquad \zeta = \frac{z}{\sqrt{4D\frac{x}{V}}}$$





The general case of diffusion with convection
Lets look at evaporation of benzene through capillary



At 6 °C, the benzene vapor is dilute, and evaporation is limited by diffusion

At 80.1 °C, the benzene boils and flows; evaporation is controlled by convection

At 60 °C, an intermediate case occurs in which both diffusion and convection are important

E. L. Cussler, in Diffusion

Separating convection from diffusion

Total mass transport $=$ mass transport by diffusion $+$ mass transport by convection

Total mass transport for component 1 $= c_1 * v_1$

c_1 = solute concentration

v_1 = solute velocity

Note that convection problems can be simplified we if refer it with respect to average reference velocity

mass transport by convection for component 1 $= c_1 * v^a$

$$v^a = v^{average} = x_1 v_1 + x_2 v_2$$

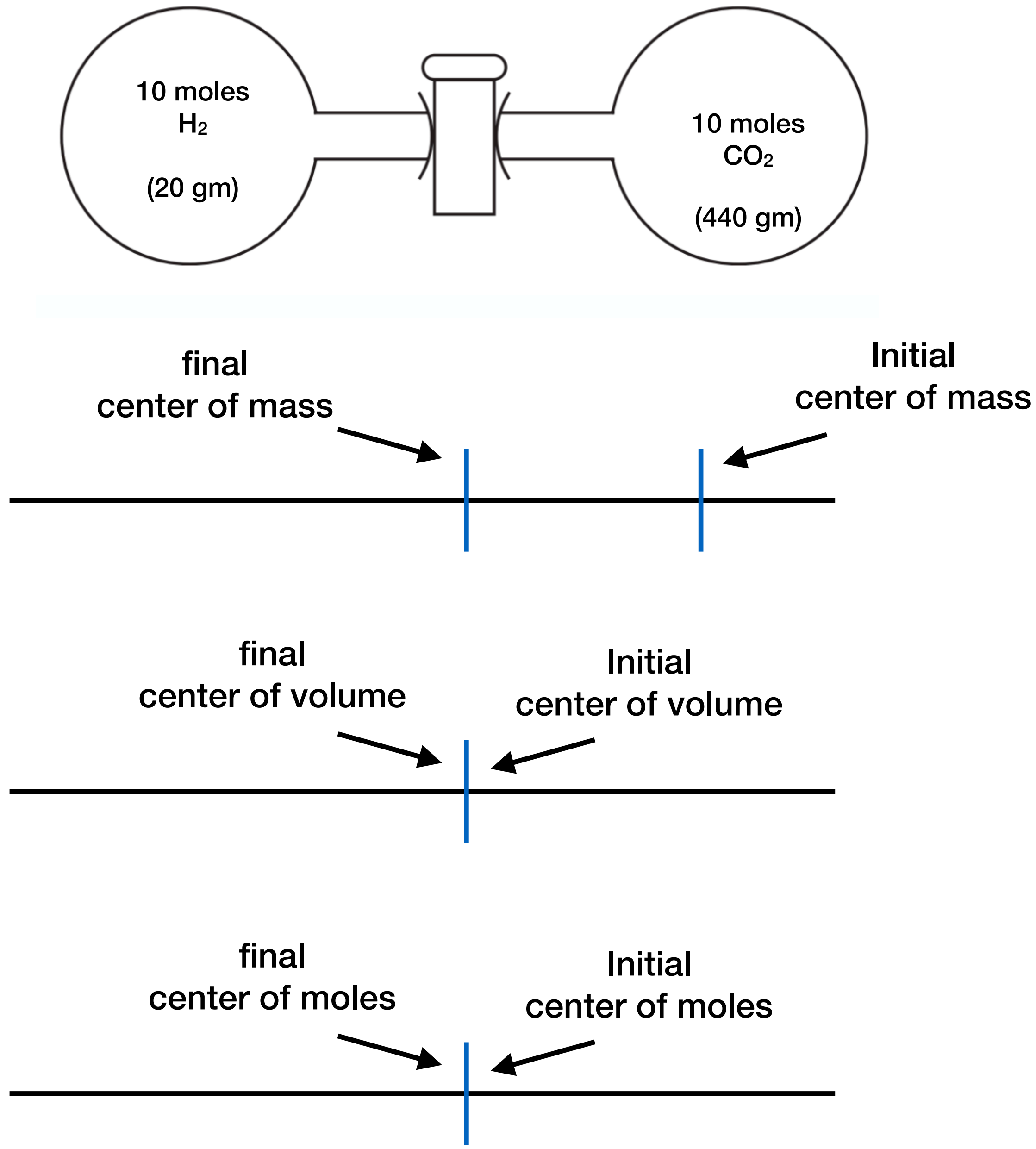
Total mass transport of component 1 $= c_1 v_1 = c_1 (v_1 - v^a) + c_1 v^a$

$$c_1 v_1 = j_1^a + c_1 v^a$$

Total mass transport $=$ mass transport by diffusion $+$ mass transport by convection

A good choice for reference velocity, v^a

Choose reference velocity v^a such that it becomes 0 or remains constant (w.r.t. position) and we are left with simple diffusion problem



$$v^m = \text{average velocity of mass} \neq 0$$

$$v^m = w_1 v_1 + w_2 v_2$$

$$v^v = \text{average velocity of volume} = 0$$

$$v^v = c_1 \bar{V}_1 v_1 + c_2 \bar{V}_2 v_2 \qquad \bar{V}_i = \frac{\partial V}{\partial N_i} = \text{molar volume}$$

$$v^v = \rho_1 \bar{V}_1 v_1 + \rho_2 \bar{V}_2 v_2 \qquad \bar{V}_i = \frac{\partial V}{\partial m_i} = \text{specific volume}$$

$$c_i \bar{V}_i = \text{volume fraction} \qquad \rho_i \bar{V}_i = \text{volume fraction}$$

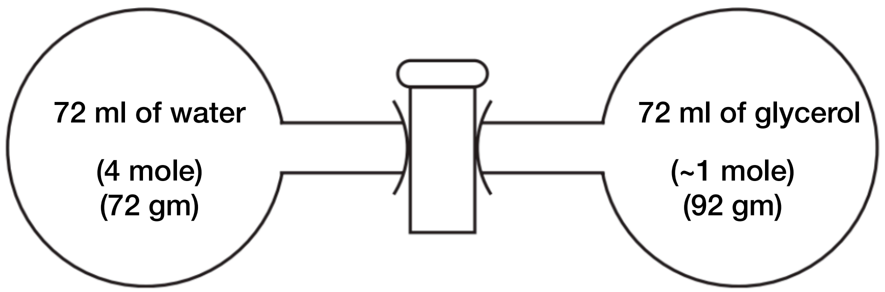
$$v = \text{average velocity of mole} = 0$$

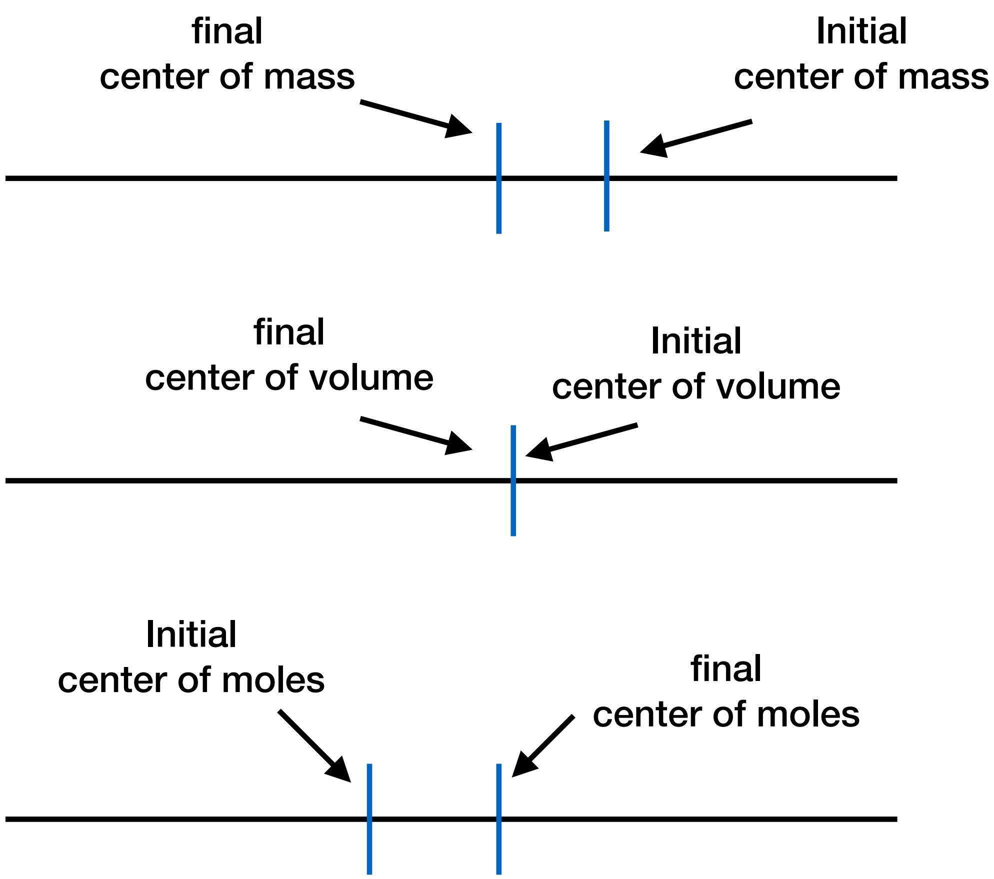
$$v = y_1 v_1 + y_2 v_2$$

In this case, we can pick v^a as either v^v or v

A good choice for reference velocity, v^a

Choose reference velocity v^a such that it becomes 0 or remains constant (w.r.t. position) and we are left with simple problem





$$v^m = \text{average velocity of mass} \neq 0$$
$$v^m = w_1 v_1 + w_2 v_2$$

$$v^v = \text{average velocity of volume} = 0$$
$$v^v = c_1 \bar{V}_1 v_1 + c_2 \bar{V}_2 v_2 \qquad \bar{V}_1 = \frac{\partial V}{\partial N_1} = \text{molar volume}$$
$$v^v = \rho_1 \bar{V}_1 v_1 + \rho_2 \bar{V}_2 v_2 \qquad \bar{V}_i = \frac{\partial V}{\partial m_i} = \text{specific volume}$$

$$v = \text{average velocity of mole} \neq 0$$
$$v = y_1 v_1 + y_2 v_2$$

In this case, we can pick v^a as v^v

The case of mole average velocity, v

Ideal for

- gases
- where total molar concentration c is constant

v = average velocity of moles

$$v = y_1 v_1 + y_2 v_2$$

$$y_1 \;=\; \text{mole fraction} = \frac{\text{mole}_1}{\text{mole}_1 \;+\; \text{mole}_2}$$

Total mole transported for 1$^{\text{st}}$ component $= \mathrm{n}_1 = \mathrm{c}_1\mathrm{v}_1 = \mathrm{c}_1\,(\mathrm{v}_1 - \mathrm{v}) + \mathrm{c}_1\mathrm{v}$

$$c_1 \;=\; \text{concentration}_1 \;=\; \frac{\text{mole}_1}{\text{volume}}$$

$$j_1 = c_1(v_1 - v) \;= -D\,\nabla c_1 \;= -Dc\,\nabla y_1$$

$$c_1 \;=\; c y_1$$

$$n_1 = j_1 + c_1 v$$

$$n \;=\; n_1 \;+\; n_2 \;=\; c_1 v_1 \;+\; c_2 v_2 \;=\; c(y_1 v_1 \;+\; y_2 v_2) \;=\; cv$$

The case of volume average velocity, v^V

Ideal for
- gases
- liquids
- Can use either molar or specific volume

v^v = average velocity of volume $\quad v^v = c_1\bar{V}_1 v_1 + c_2\bar{V}_2 v_2 = \bar{V}_1 n_1 + \bar{V}_2 n_2$ $\quad \bar{V}_1 = \frac{\partial V}{\partial N_1}$ = molar volume

Alternate definition $\quad v^v = \rho_1\bar{V}_1 v_1 + \rho_2\bar{V}_2 v_2 = \bar{V}_1 n_1 + \bar{V}_2 n_2$ $\quad \bar{V}_1 = \frac{\partial V}{\partial m_1}$ = specific volume

Total mole transported for component 1 $= n_1 = c_1 v_1 = c_1 (v_1 - v^v) + c_1 v^v$

$$c_1 = \text{concentration}_1 = \frac{\text{mole}_1}{\text{volume}}$$

$$j_1^v = c_1(v_1 - v^v) = -D\nabla c_1$$

$$c_1 = c y_1$$

c may not be uniform

$$n_1 = j_1^v + c_1 v^v$$

EPFL

Overall, comparison

Molar $v = y_1 v_1 + y_2 v_2$ $\quad n_1 = j_1 + c_1 v$ $\quad j_1 = c_1(v_1 - v)$ $\quad n = n_1 + n_2 = cv$

$$= -Dc\nabla y_1$$

Volume $v^v = c_1 \bar{V}_1 v_1 + c_2 \bar{V}_2 v_2$ $\quad n_1 = j_1^v + c_1 v^v$ $\quad j_1^v = c_1(v_1 - v^v)$

$$= -D\nabla c_1$$

$$\bar{V}_i = \frac{\partial V}{\partial N_i} = \text{molar volume}$$

v = average velocity of moles

v^v = average velocity of volumes

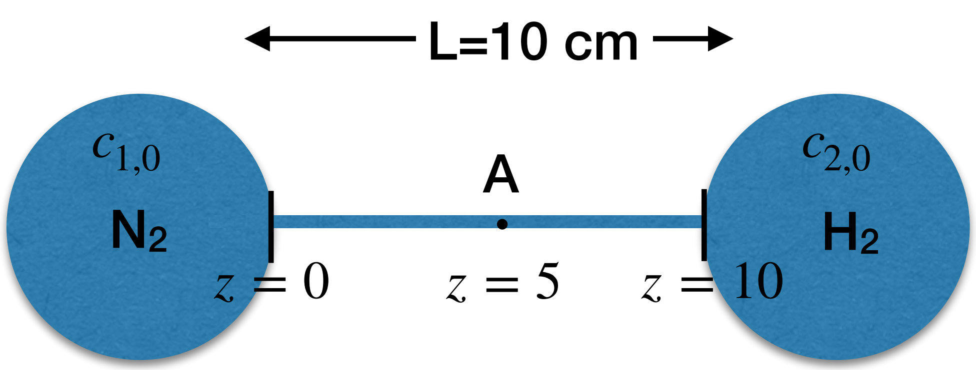
Volume average is overall best

- System with constant molar concentration, $v^v = v$ using molar conc.

In class exercise problem

In the diffusion apparatus shown here, a large, well-mixed and infinitely large N_2 reservoir is separated from an infinitely large, well-mixed H_2 reservoir using a small tube with length of 10 cm. D for H_2 is 0.1 cm²/s and for N_2 is 0.1 cm²/s. Calculate mass, molar and volume average velocities at point A at the steady state. Also calculate the flux of N_2 at point A.

N_2 is species 1, H_2 is species 2



$$v = \text{average velocity of moles} \ = \ 0$$

$$v^v = \text{average velocity of volumes} \ = \ 0$$

$$v^m = \text{average velocity of mass} \ \neq \ 0 \ = \ \mathrm{w}_1\mathrm{v}_1 + \mathrm{w}_2\mathrm{v}_2$$

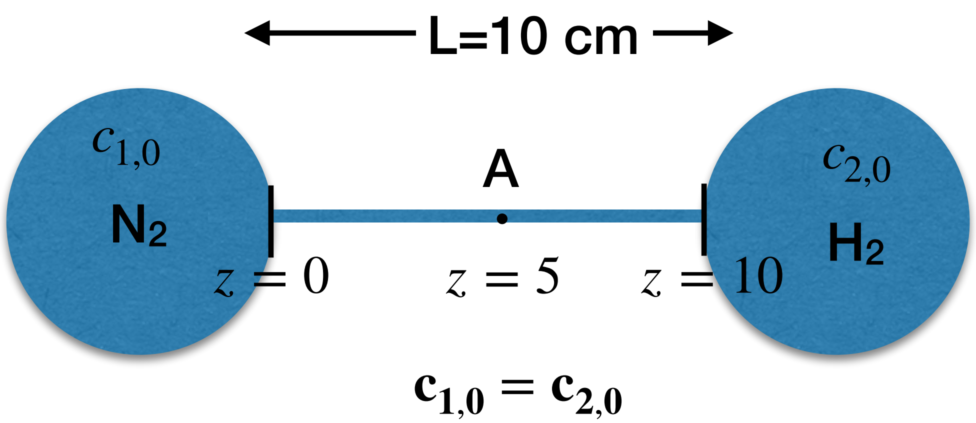
$$\mathbf{c_{1,0} = c_{2,0}}$$

Using average velocity of moles is convenient because it is zero

Because the transport is purely diffusive in our reference, we can use the thin film results

$$c_{1,A} = \frac{c_{1,0}}{2}$$

$$j_1 = D_1 \frac{c_{1,0}}{L}$$

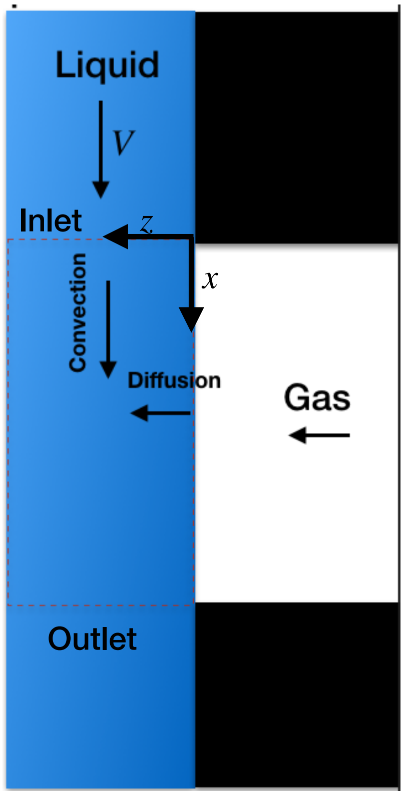


Exercise problem 1: Carbon capture by falling amine film

A promising technique to remove carbon dioxide is to trap it in a falling amine film by absorption. Consider a 1 m tall falling pure amine film contacted with CO_2 at the surface, immediately reaching saturation at the surface (z = 0). Calculate the minimum diffusion coefficient, D, needed to achieve a CO_2 concentration that is at least 50% of its saturation value at the outlet (x = 1 m) of the stream (bottom) at z (depth inside film) = 1 cm.

The film is falling with a velocity of 1 cm/s.

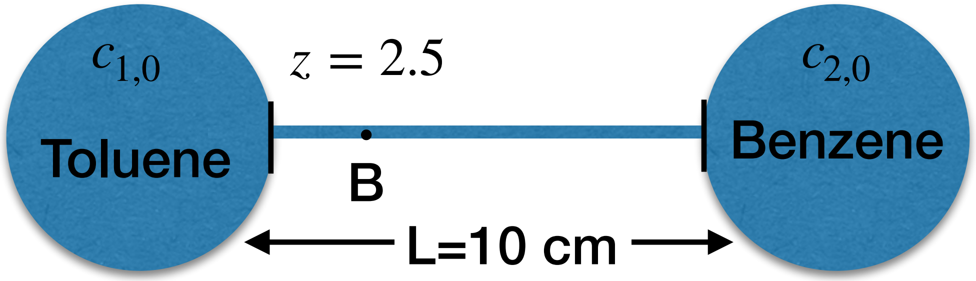
x and z are specified; x = 1 m, z = 1 cm (outlet)



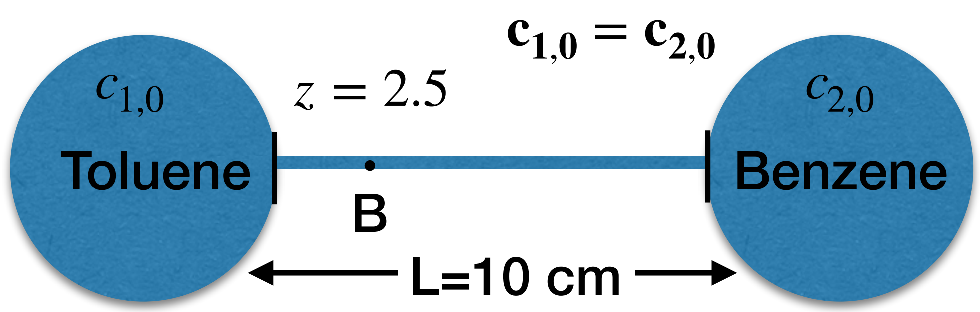
Exercise problem 2

In the diffusion apparatus shown here, an infinitely large, well-mixed toluene reservoir is separated from an infinitely large, well-mixed benzene reservoir using a small tube with length of 10 cm. D is same for both liquids and is 10^{-4} cm^2/s. Calculate mass and molar average velocities at points B at the steady state. Assume volume average velocity to be zero.

toluene is species 1, benzene is species 2



$\mathbf{c_{1,0} = c_{2,0}}$


$\mathbf{c_{1,0} = c_{2,0}}$
$c_{1,0}$
Toluene
$z = 2.5$
B
L=10 cm
$c_{2,0}$
Benzene